Available online at www.sciencedirect.com

ScienceDirect

Procedia Earth and Planetary Science 10 (2014) 149 – 153

Procedia
Earth and Planetary Science

Geochemistry of the Earth's Surface meeting, GES-10

The oxidative dissolution of FeS at pH 2.5 in the presence of ethylenediaminetetraacetate (EDTA)

Paul Chiriţă[a]*, Mădălina I. Duinea[a], Cătălina Bădică[a], Michel L. Schlegel[b,c]

[a]*University of Craiova, Department of Chemistry, Calea Bucuresti 107I, Craiova, Romania*
[b]*CEA, DEN, DPC/SEARS/LISL, F-91191 Gif-sur-Yvette, France*
[c]*University of Evry, UMR 8587 LAMBE, F 91 025 Evry, France*

Abstract

The effect of ethylenediaminetetraacetate (EDTA) on the oxidative dissolution of FeS at pH 2.5 and 25 °C was investigated by using potentiodynamic polarization technique and electrochemical impedance spectroscopy. The results of our study show that EDTA affects aqueous oxidation of FeS. It exerts two opposite effects on the anodic process: 1) a promoting effect, because of the dissolution of ferric (oxyhydr)oxides, and 2) an inhibiting effect, because of EDTA adsorption on FeS surface.

Peer-review under responsibility of the Scientific Committee of GES-10

Keywords: FeS oxidation; EDTA; PP; EIS

1. Introduction

Iron monosulfide minerals (pyrrhotite, troilite and mackinawite) are more reactive than iron disulfide phases (pyrite and marcasite). In contact with oxygen-bearing solutions they easily oxidize and result in acid mine drainage, along with other mineral sulfides.[1,2] Their oxidation starts with non-oxidative dissolution (a proton consuming reaction) and continues with the oxidation of S(-II) and Fe(II).[3] Sulfur(-II) can be oxidized to polysulfide, elemental sulfur and sulfoxyanions. Iron(II) is oxidized to Fe(III). At high pH values, Fe(III) ions precipitate as ferric

* Corresponding author. Tel.: +40-251-597-048; fax: +40-251-597-048.
E-mail address: paulxchirita@gmail.com

Peer-review under responsibility of the Scientific Committee of GES-10
doi:10.1016/j.proeps.2014.08.048

(oxyhydr)oxides. Polysulfide, elemental sulfur and ferric (oxyhydr)oxides form a surface layer that alters the oxidative dissolution of FeS minerals.[3,4] The ligands which react with Fe(III) are expected to influence the aqueous oxidation of FeS. On the one hand, they can alter the surface layer and increase the rate of FeS oxidative dissolution. On the other hand, they may be interposed between the oxidized surface and solution by forming co-ordination bonds with surface iron. In this way they act as inhibitors of FeS oxidation.

In this study we have investigated the effect of ethylenediaminetetraacetate, a ligand of Fe(III), on the oxidative dissolution of FeS using potentiodynamic polarization technique and electrochemical impedance spectroscopy. Ethylenediaminetetraacetate contaminates certain sites due to its industrial use as a powerful ligand for metals like Ca, Zn, Pb or Fe(III)[5] and consequently can affect the oxidative dissolution of FeS.

2. Experimental

Synthetic iron(II) sulfide obtained from Merck was used in the study. X-ray diffraction analysis (Philips PW3710 diffractometer, CuKα) showed that the iron sulfide phase is troilite (FeS). Aqueous solutions were prepared with distilled water and chemicals of reagent grade purity.

The electrochemical behavior of the FeS in the absence and presence of ethylenediaminotetraacetate (EDTA) was studied by potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) using a three-electrode cell filled with air-equilibrated HCl solutions at pH 2.5 and at 25 ^{o}C. The working electrode was a rectangular FeS sample with the apparent exposed surface area of 1 cm^2. Prior to each run, the working electrode was polished with 600, 2000 and 3000 grade SiC paper, degreased in ethyl alcohol, dried and then immersed in the experimental solution. The counter-electrode was a platinum foil. The working electrode potentials were recorded versus a saturated calomel electrode (SCE). An electrochemical workstation Zahner interfaced with a PC and controlled by Thales software was used for measurements. The potentiodynamic polarization curves were recorded at a potential scan rate of 1 mV/s. The potential range was from -0.25 to 0.25 V versus open circuit potential (OCP). Electrochemical impedance measurements were performed in the frequency range of 10 mHz to 3 MHz with an ac perturbation voltage of 10 mV to study the FeS/solution interface. All potentials presented in this paper are expressed against standard hydrogen electrode (SHE).

3. Results and discussion

Fig. 1 shows the potentiodynamic polarization curves of FeS electrode in aqueous solutions at 25 ^{o}C and pH 2.5 in the absence and at increasing concentrations of EDTA. The variation of cathodic current densities was insignificant when the total concentration of EDTA ($[EDTA]_{tot}$) increases from 0 up to 1 mM. A more important variation was observed in the case of anodic current densities (insert in Fig. 1). It is important to note that when EDTA was added to HCl solutions, the current density recorded at the end of anodic curves (Table 1) increased from 611 μA cm^{-2} (0 mM) up to 671 μA cm^{-2} (0.1 mM). A subsequent increase in $[EDTA]_{tot}$ caused a decrease in current density recorded at the end of anodic curves (E≈-130 mV) down to 542 μA cm^{-2} (0.75 mM). This behavior indicates that the overall effect of EDTA is the sum of two opposite effects: (1) a promoting effect ($[EDTA]_{tot} \leqslant 0.5$ mM) that can be attributed to the dissolution of ferric (oxyhydr)oxydes present on FeS surface in the presence of EDTA, and (2) an inhibiting effect ($[EDTA]_{tot} > 0.5$ mM) that can be due to the interaction of EDTA and iron incorporated in the surface layer developed on FeS surface.

Values of OCP (Table 2) show some limited variations around the average value of -384 mV when $[EDTA]_{tot}$ increases from 0 to 1 mM.

The impedance behavior of FeS electrode in air-equilibrated HCl solutions at pH 2.5 and 25 ^{o}C in the absence and at increasing $[EDTA]_{tot}$ is presented in Fig. 2. The Nyquist plots show two capacitive loops indicating the presence of two main time constants. The capacitive loops at low frequencies are depressed in nature having their center below the abscissa. A possible explanation of this behavior is the presence of inhomogeneities of the FeS/solution interface formed during oxidation.[6,7] It important to note that the radius of the capacitive loops at low frequencies is very similar for all $[EDTA]_{tot}$ values (in the range 0-1 mM). The capacitive loops at low frequencies are the result of the charge transfer process of electrochemical reactions produced during FeS oxidation.[8] The capacitive loops

present at high frequencies can be attributed to mass transfer across the layer (composed by elemental sulfur, ferric (oxyhydr)oxides and adsorbed EDTA) present on FeS surface.

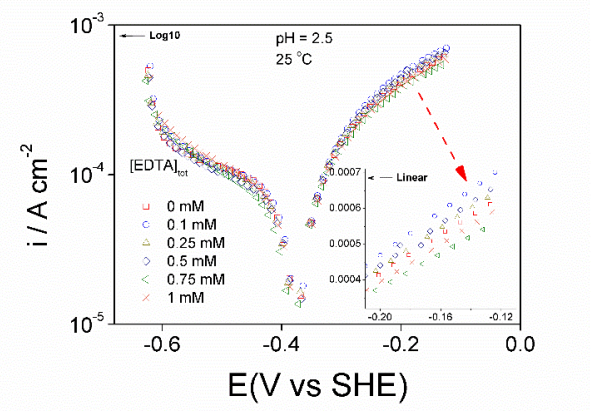

Fig. 1. Potentiodyamic polarization curves for FeS electrodes in air-equilibrated HCl solutions at pH 2.5 and 25 °C.

Table 1. Current densities recorded at a potential of ≈-130 mV vs SHE (the end of anodic curves).

$[EDTA]_{tot}$ / mM	i / µA cm^{-2}
0	611
0.1	671
0.25	630
0.5	653
0.75	542
1	589

Table 2. OCP values of FeS immersed in HCl solutions with different EDTA concentrations.

$[EDTA]_{tot}$ / mM	OCP / mV vs SHE
0	-381.4
0.1	-383.1
0.25	-379.9
0.5	-381.8
0.75	-391.9
1	-388.2

The micrographs of unreacted FeS and FeS reacted in the absence and presence of EDTA are shown in Figs. 3A-D. Fig. 3A shows that on the surface of unreacted FeS there are only grooves caused by polishing. For FeS oxidatively dissolved in absence of EDTA, the surface locally becomes reddish-brown, suggesting the growth of ferric (oxyhydr)oxides (Figs. 3B). When EDTA was added into HCl solutions these reddish-brown deposits disappeared and evidence of extensive oxidative dissolution appeared (Figs. 3C and D). Additionally the grooves caused by polishing disappeared on the surface of FeS. These observations suggest that EDTA promotes the oxidative dissolution of FeS by initially dissolving ferric (oxyhydr)oxides formed on the mineral surface. However, as the electrochemical data indicate, at high values of ligand concentration, the adsorption of EDTA on mineral

surface controls the aqueous oxidation of FeS. The adsorbed EDTA inhibits the aqueous oxidation of FeS hindering the electron transfer from FeS to oxidant.

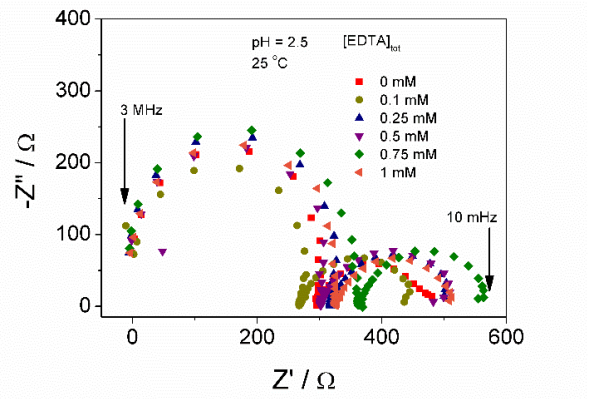

Fig. 2. Nyquist plots of FeS electrodes in air-equilibrated solutions at pH 2.5 and 25 °C, in the presence and absence of EDTA.

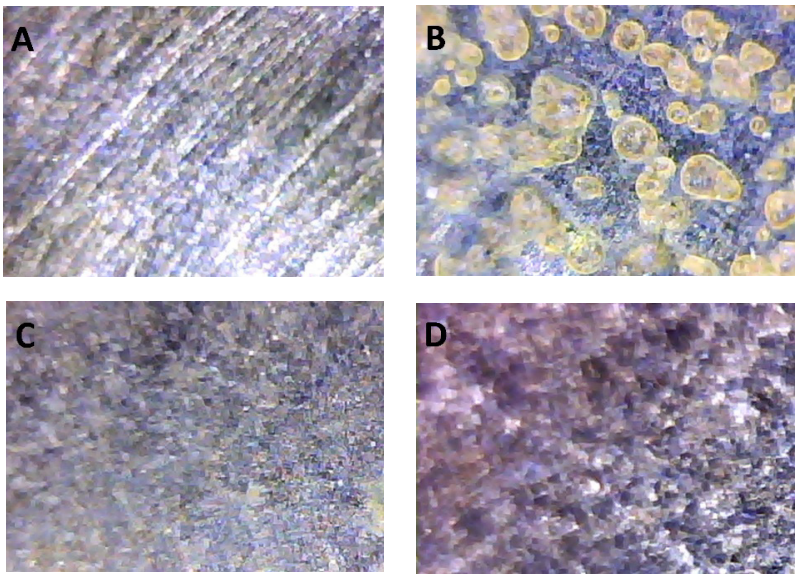

Fig. 3. Micrograph (x200) of (A) unreacted FeS electrode and FeS electrode reacted in the (B) absence and presence of (C) 0.1 mM EDTA and (D) 1 mM EDTA at pH 2.5 and 25 °C.

4. Conclusions

It was found that EDTA (and possibly other ligands of the ferric iron) present at contaminated sites affects aqueous oxidation of FeS (anodic reaction). Electrochemical analysis of FeS electrode shows two capacitive loops. The loop at low frequencies is the result of the charge transfer process of electrochemical reactions produced during FeS oxidation, and the capacitive loop presents at high frequencies can be attributed to mass transfer across the surface layer. The microscopic inspection of reacted electrodes coupled with the results of electrochemical measurements indicate that EDTA exerts two opposite effects: 1) a promoting effect, because of the dissolution of ferric (oxyhydr)oxides, and 2) an inhibiting effect, because of EDTA adsorption on FeS surface.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI, project number 51/2012.

References

1. Belzile N, Chen YW, Cai MF, Li Y. A review on pyrrhotite oxidation. *J Geochem Explor* 2004; **84**: 65-76.
2. Chirita P, Rimstidt JD. Pyrrhotite dissolution in acidic media. *Appl Geochem* 2014; **41**: 1-10.
3. Chirita P, Descostes M, Schlegel ML. Oxidation of FeS by oxygen-bearing acidic solutions. *J Colloid Interface Sci* 2008; **321**: 84-95.
4. Chirita P, Schlegel ML. Reaction of FeS with Fe(III)-bearing acidic solutions. *Chem Geol* 2012; **334**: 131-138.
5. Nowack B, Sigg L. Dissolution of Fe(III) (hydr) oxides by metal-EDTA complexes. *Geochim Cosmochim Acta* 1997; **61**: 951-963.
6. Yıldız R, Dogan T, Dehri I. Evaluation of corrosion inhibition of mild steel in 0.1 M HCl by 4-amino-3-hydroxynaphthalene-1-sulphonic acid. *Corros Sci* 2014; **85**: 215-221.
7. Jeyaprabha C, Sathiyanarayanan S, Venkatachari G. Effect of cerium ions on corrosion inhibition of PANI for iron in 0.5 M H_2SO_4. *Appl Surf Sci* 2006; **253**: 432-438.
8. Tuken T, Yazici B, Erbil M. The corrosion behaviour of polypyrrole coating synthesized in phenylphosphonic acid solution. *Appl Surf Sci* 2006; **252**: 2311-2318.